

Equivalent WO 95 13340



to EP 728172

#13

PCT

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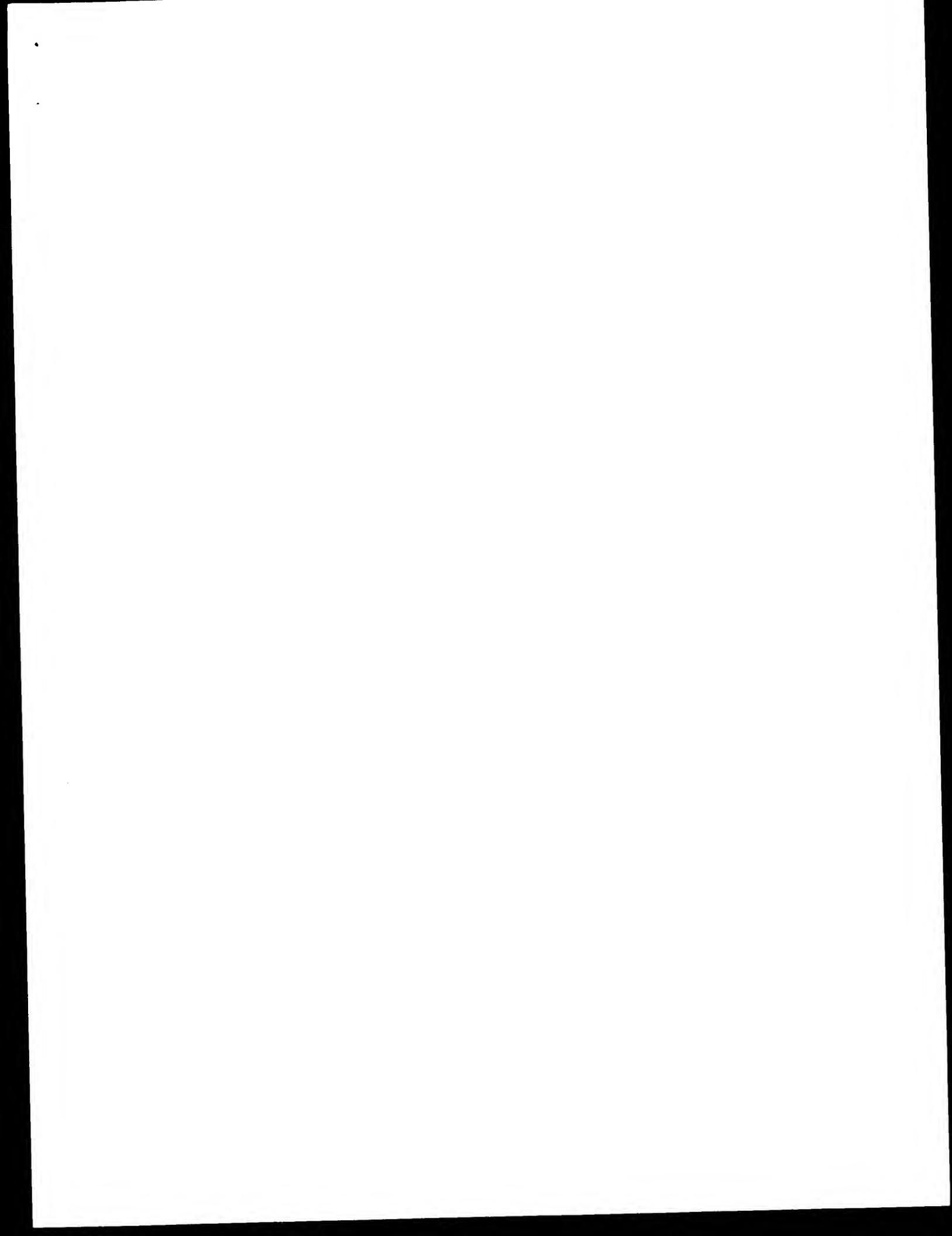
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C10K 1/20, B01D 53/68	A1	(11) International Publication Number: WO 95/13340 (43) International Publication Date: 18 May 1995 (18.05.95)
(21) International Application Number: PCT/EP94/03699		(81) Designated States: AU, CA, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 8 November 1994 (08.11.94)		
(30) Priority Data: 153,591 12 November 1993 (12.11.93) US		Published <i>With international search report.</i>
(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandstraat 30, NL-2596 HR The Hague (NL).		
(72) Inventors: MAHAGAOKAR, Uday; 12246 Villa Lea, Houston, TX 77071 (US). DOERING, Egon, Lorenz; 2611 Williamsburg, Pasadena, TX 77502 (US). UNGER, Phillip, Edward; 10 Shadow Lane, Houston, TX 77080 (US). VAN DEN BERG, Franciscus, Gondulfus, Antonius; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		

(54) Title: **A METHOD OF REDUCING HYDROGEN HALIDE(S) CONTENT IN SYNTHESIS GAS**

(57) Abstract

A method for reducing the hydrogen halide(s) content of a synthesis gas stream by gasifying a carbonaceous feed material in a gasifier to produce a gas/solids mixture of hydrogen, carbon monoxide, hydrogen halide gas, and fly slag particles; passing the gas/solids mixture to a solids removal zone where at least a portion of the fly slag particles are removed, to produce a gas stream; admixing with the said gas stream an alkali metal oxide, hydroxide, bicarbonate, or carbonate to produce an alkali metal compound/gas mixture; passing the alkali metal compound/gas mixture to a means for increasing the contact time between said hydrogen halide(s) and said alkali metal compound(s) or their thermal decomposition products; reacting the alkali metal compound(s) with the said hydrogen halide(s) to produce solid alkali metal halide(s); and recovering a gas stream substantially free of hydrogen halide(s) and solids.



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A METHOD OF REDUCING HYDROGEN HALIDE(S) CONTENT IN SYNTHESIS GAS

The invention relates to a method for reducing hydrogen halide(s) content, in particular hydrogen chloride content, of a synthesis gas stream.

The combustion of a carbonaceous material such as a solid carbonaceous fuel by reaction with a source of gaseous oxygen is well known. In such a reaction, an amount of air or oxygen equal to or greater than that required for complete combustion is used, whereby the gaseous effluent contains carbon dioxide with little, if any, carbon monoxide. It is also known to carry out the 5 gasification or partial oxidation of solid carbonaceous materials or fuels employing a limited quantity of oxygen or air so as to produce primarily carbon monoxide and hydrogen.

Fuel sources, in particular coals, often have an undesirable halide(s) content. The halogens in the halides, in particular chlorine in chlorides and fluorine in fluorides, form acids in the 10 synthesis gas mixture which can cause severe corrosion in the downstream processing equipment. The halides also pose environmental and safety hazards if emitted to the atmosphere.

Another problem caused by the halides is reduced efficiency of 15 the gasification process. Condensation of some salts in the synthesis gas during cooling limits the overall efficiency of the heat recovery from the synthesis gas. This limitation in heat recovery occurs because some moderate sublimation temperature salts, such as ammonium chloride, are very corrosive when permitted to 20 condense. Thus, to avoid having the salts condense, the synthesis gas cannot be cooled below the sublimation temperature of various salts. Since the temperature to which the synthesis gas may be cooled is thus limited, the heat recovery from the gas is accordingly limited. In particular, chlorine-containing salts are 25 formed due to the presence of HCl. By removing HCl from the 30

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synthesis gas, formation of such salts in the gas stream is reduced or eliminated and the gas can be cooled further to permit more thermal recovery.

A prior known method of removing HCl is by a wet absorption system. In this known method the synthesis gas must be cooled and passed through an aqueous absorption column. The HCl is absorbed in the water and neutralized with NaOH. This method has drawbacks since cooling the gas to remove the HCl is inefficient and results in heat/energy loss. Also, additional equipment costs and maintenance costs result from the addition of an absorption column to the process. Economic drawbacks also result from the need for a large water treatment plant due to a build-up of salts in the water from the absorption column.

It is known from U.S. Patent Specification No. 5,118,480 to add metal-containing compounds such as nahcolite to a synthesis gas downstream of the gasifier to remove HCl in conjunction with removing sulphur with a metal oxide sorbent. However, this process fails to address the problem of high expense associated with long piping necessary to have sufficient residence time for complete reaction.

It is therefore an object of the present invention to provide a practical and economical dry method of reducing the hydrogen halide(s) content of synthesis gas, without the high expense of long piping.

The invention provides a method for reducing the hydrogen halide(s) content of a synthesis gas stream comprising the steps of:

- (a) gasifying a carbonaceous feed material in a gasifier under gasifying conditions thereby producing a gas/solids mixture comprising hydrogen, carbon monoxide, one or more hydrogen halides, and fly slag particles;
- (b) passing the said gas/solids mixture to a solids removal zone wherein at least a portion of the fly slag particles are removed, thereby producing a gas stream;
- (c) admixing with the said gas stream obtained in step (b) at least an alkali metal compound, thereby producing an alkali metal

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compound/gas mixture;

(d) passing the said alkali metal compound/gas mixture obtained in step (c) to a means for increasing the contact time between the hydrogen halide(s) and the alkali metal compound(s) or their thermal decomposition products;

5 (e) reacting the alkali metal compound(s) or thermal decomposition products thereof, with the hydrogen halide(s) thereby producing solid alkali metal halide(s), wherein a cake of solids builds up on the surface of the said means for increasing the contact time between the hydrogen halide(s) and the alkali metal compound(s) or their thermal decomposition products;

10 (f) periodically removing at least a portion of the cake of solids; and

(g) recovering from the said means for increasing the contact time between the hydrogen halide(s) and the alkali metal compound(s) or their thermal decomposition products a gas stream substantially free of hydrogen halide(s).

The invention will now be described in more detail by way of example by reference to specific process aspects thereof.

20 A. Feeds and alkali metal Compounds and Mixture Thereof

Several types of carbonaceous materials are suitable as feed sources for gasification. These include bituminous coal, sub-bituminous coal, anthracite coal, lignite, liquid hydrocarbons, petroleum coke, various organic scrap materials, municipal refuse, solid organic refuse contaminated with radioactive materials, paper industry refuse, and photographic scrap. Coal and petroleum coke are considered advantageous feeds.

25 The alkali metal compounds include for example potassium oxide, potassium hydroxide, potassium bicarbonate, potassium carbonate, sodium oxide, sodium hydroxide, sodium bicarbonate, and sodium carbonate. Nahcolite, a naturally occurring form of sodium bicarbonate, is advantageously applied for its economy and availability. The alkali metal compounds are optionally used individually or in combination.

30 35 The alkali metal compounds are mixed with the synthesis gas

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after the synthesis gas leaves the gasifier. Advantageously, an entrained flow gasifier is applied. The alkali metal compound is injected, advantageously dry, into the synthesis gas stream in any way suitable for the purpose. It is transported pneumatically in 5 nitrogen or carbon dioxide or in any other conventional dry feed manner. Advantageously, at least a portion of the sensible heat of the synthesis gas is recovered prior to adding the alkali metal compound. More in particular, the synthesis gas passes through a first heat recovery zone, a solids removal zone, then a second heat 10 recovery zone, and then the alkali metal compound is injected into the gas stream recovered from the second heat recovery zone.

The solids removal stage is advantageously a cyclone or ceramic candle filter, used individually or in combination. An electrostatic precipitator is optionally used where the system 15 pressure is at or near atmospheric. Advantageously, the maximum amount of sensible heat is recovered which does not reduce the temperature of the synthesis gas below the condensation point of any chloride compounds present in the synthesis gas. Such condensation results in equipment corrosion problems.

20 B. Reaction, Cooling, and Solids Removal

By way of example reference will in particular be made to the dry removal of hydrogen chloride from synthesis gas. However, it will be appreciated by those skilled in the art that the method of the invention is also applicable for removal of other hydrogen 25 halide(s) from synthesis gas.

After the alkali metal compound is injected it will react with the halogen e.g. chlorine in the hydrogen halide e.g. hydrogen chloride to form a solid salt. The alkali metal compound either reacts directly with the hydrogen halide or the alkali metal compound may first thermally decompose prior to such reaction. 30 Where the alkali metal compound is a sodium compound, e.g., sodium bicarbonate, sodium halide is formed. The resulting alkali metal halide is a solid.

The solid-salt-containing synthesis gas stream then passes to a 35 means for increasing the contact time between the hydrogen halide(s)

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and the alkali metal compound(s) e.g. a (ceramic candle) filter. Additionally, much of the reaction between the alkali metal compound and the hydrogen halide occurs on the upstream surface of the (ceramic candle) filter. This is because the residence time between the point of alkali metal compound injection and the filter will typically be too short for complete reaction. Extension of the pathway to increase the residence time would be uneconomical.

A cake of salt solids builds up on the surface of the (ceramic candle) filter. For the synthesis gas to get through the cake to exit the filter, it must travel a convoluted pathway through the solids cake. Thus, the contact time between the hydrogen halide(s) and the alkali metal compound(s) or their thermal decomposition products is increased to provide a longer effective residence time without the uneconomical expense of lengthening the piping.

The synthesis gas recovered from the (ceramic candle) filter has reduced amounts of hydrogen halides, e.g. hydrogen chloride, and is advantageously substantially free of hydrogen halides, e.g. hydrogen chloride. Advantageously, the synthesis gas is then passed to a third heat recovery zone, to maximize sensible heat recovery before passing the synthesis gas to any wet cleanup units, such as a sulphur removal scrubbing unit.

C. Concentrations of Halides, Ratios, and Percent Removal

In the reducing atmosphere and elevated temperatures of the gasifier, a halide such as chloride in the coal evolves into hydrogen chloride. The initial concentrations of hydrogen chloride and other hydrogen halides in the synthesis gas vary widely with the type and source of the feed to the gasifier. Chloride concentrations in coal range from about 0.01% by weight chlorine to about 0.35% by weight chlorine. Other halide concentrations in coal are typically much lower than chloride concentrations.

At least a stoichiometric amount of alkali metal compounds must be mixed with the synthesis gas with respect to the halide concentration in the synthesis gas. Advantageously, one to three times the stoichiometric ratio is used of alkali metal compounds to halides such as chlorides. This assures a high degree of removal of

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the chlorides. More than about three times the stoichiometric ratio is wasteful of alkali metal compounds and makes the process uneconomical without any apparent benefit.

From about 95% by weight to about 99% by weight of the halides such as chlorides, are removed in the practice of this method. For example, the synthesis gas will initially contain from about 10 ppm by volume (ppmv) to about 1000 ppmv chloride where the feed is coal. After gasification and reaction and solids removal of the metal halides, the concentration of chloride in the synthesis gas is from about 0.1 ppmv to about 5 ppmv.

D. Operating Conditions

The gasifier is advantageously an entrained flow gasifier and is operated at gasifying conditions. These conditions are known to an expert and may vary from feed to feed. The temperature is a temperature high enough to gasify a substantial portion of the carbonaceous feed and to prevent the formation of undesirable side-products, such as tars and phenols and other aromatics. Typical temperatures in the gasifier are from about 1100°C to about 2000°C. Where the feed is coal, the gasifier temperature is advantageously from about 1450°C to about 1575°C. More in particular, the temperature is from about 1475°C to about 1510°C. The pressure of the gasifier is from about 14 bar to about 42 bar. Advantageously, the pressure is from about 21 bar to about 31.5 bar.

At the point of injection of the alkali metal compound the synthesis gas temperature is above the point at which any corrosive ammonium halide compounds, such as ammonium chlorides, will condense. This temperature varies with the type and concentration of halide compound. This is typically at least about 150 °C. The temperature at the point of injection, however, is advantageously not above the condensation point of sodium chloride. This is typically below about 670 °C. This limitation is necessary since sodium chloride must be a solid to be removed by the (ceramic candle) filter. It is not essential, however, that the temperature at the point of injection be above the point of condensation of sodium chloride, so long as the mixture reaches this temperature

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prior to reaching the upstream surface of the (ceramic candle) filter. Advantageously, the temperature of the synthesis gas stream at the point of alkali metal compound injection is from about 180 °C to about 370 °C, more in particular from about 230 °C to about 260 °C.

5 Various modifications of the present invention will become apparent to those skilled in the art from the foregoing description. Such modifications are intended to fall within the scope of the appended claims.

C L A I M S

1. A method for reducing the hydrogen halide(s) content of a synthesis gas stream comprising the steps of:
 - (a) gasifying a carbonaceous feed material in a gasifier under gasifying conditions thereby producing a gas/solids mixture comprising hydrogen, carbon monoxide, one or more hydrogen halides, and fly slag particles;
 - (b) passing the said gas/solids mixture to a solids removal zone wherein at least a portion of said fly slag particles are removed, thereby producing a gas stream;
 - 10 (c) admixing with the said gas stream obtained in step (b) at least an alkali metal compound, thereby producing an alkali metal compound/gas mixture;
 - (d) passing the said alkali metal compound/gas mixture obtained in step (c) to a means for increasing the contact time between the said hydrogen halide(s) and the said alkali metal compound(s) or their thermal decomposition products;
 - 15 (e) reacting said alkali metal compound(s), or thermal decomposition products thereof, with said hydrogen halide(s) thereby producing solid alkali metal halide(s), wherein a cake of solids builds up on the surface of the said means for increasing the contact time between the said hydrogen halide(s) and the said alkali metal compound(s) or their thermal decomposition products;
 - 20 (f) periodically removing at least a portion of said cake of solids; and
 - (g) recovering from the said means for increasing the contact time between the said hydrogen halide(s) and the said alkali metal compound(s) or their thermal decomposition products a gas stream substantially free of hydrogen halide(s).
- 30 2. The method as claimed in claim 1 wherein the carbonaceous feed material is coal or petroleum coke.

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3. The method as claimed in claim 2, wherein the carbonaceous feed material is bituminous coal or sub-bituminous coal.
4. The method as claimed in any one of claims 1-3, wherein the amount of alkali metal compound(s) admixed with the effluent of said solids removal zone is at least a stoichiometric amount of alkali metal compounds with respect to the hydrogen halide(s) content of the synthesis gas.
5. The method as claimed in claim 4, wherein the amount of alkali metal compound(s) admixed with the effluent of said solids removal zone is not more than about 3 times the stoichiometric amount of alkali metal compounds with respect to the hydrogen halide(s) content of the synthesis gas.
10. The method as claimed in any one of claims 1-5, wherein said admixing step (c) consists essentially of injecting said alkali metal compound into said effluent of said solids removal zone.
15. The method as claimed in any one of claims 1-6, wherein in admixing step (c) the said alkali metal compound is dry at the point of admixture.
20. The method as claimed in any one of claims 1-7, wherein at least a portion of the sensible heat of the gas/solids mixture is recovered prior to adding the alkali metal compound.
25. The method as claimed in claim 8, wherein the gas/solids mixture is passed through a first heat recovery zone, a solids removal zone, then a second heat recovery zone, and then the alkali metal compound is injected into the gas stream recovered from the second heat recovery zone.
30. The method according to any one of claims 1-9, wherein the temperature in the gasifier is from about 1100°C to about 2000°C.
11. The method according to any one of claims 1-10, wherein the pressure in the gasifier is from about 14 bar to about 42 bar.
35. The method as claimed in any one of claims 1-11, wherein the said means for increasing the contact time is a filter.
12. The method as claimed in any one of claims 1-12, wherein the filter is a ceramic candle filter.
13. The method as claimed in claim 12, wherein the filter is a ceramic candle filter.
14. The method as claimed in any one of claims 1-13, wherein the

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alkali metal compound comprises at least one oxide, hydroxide, bicarbonate or carbonate of an alkali metal.

15. The method as claimed in any one of claims 1-14, wherein the alkali metal is sodium or potassium.

5 16. The method as claimed in any one of claims 1-15, wherein the substantially hydrogen-halide-free gas stream is passed to a third heat recovery zone wherein a portion of the sensible heat of the said substantially hydrogen-halide-free gas stream is recovered.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP 94/03699

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10K1/20 B01D53/68

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D C10K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB,A,2 106 532 (VEREINIGTE ELEKTRIZITATSWERKE WESTFALEN AG) 13 April 1983	1,7,12, 14,15
A	see page 2, line 90 - line 110; claims 1-8; figure 1 ---	2,3,5,8, 9
Y	EP,A,0 468 540 (THE BABCOCK & WILCOX COMPANY) 29 January 1992 see the whole document ---	1,7,12, 14
Y	EP,A,0 463 367 (GENERAL ELECTRIC ENVIRONMENTAL SERVICES) 2 January 1992 cited in the application see claims 1-16 ---	15
		-/-

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Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

7 February 1995

23.02.95

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NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax. (+ 31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 94/03699

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	EP,A,0 573 209 (FOSECO INTERNATIONAL LIMITED) 8 December 1993 see the whole document ---	1,6,7, 12,13
A	EP,A,0 314 253 (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ) 3 May 1989 ----	1,10-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP 94/03699

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-2106532	13-04-83	DE-A-	3137812	31-03-83
		JP-C-	1442135	30-05-88
		JP-A-	58067323	21-04-83
		JP-B-	62048527	14-10-87
		US-A-	4472363	18-09-84
EP-A-0468540	29-01-92	US-A-	4793981	27-12-88
		CA-A-	1273474	04-09-90
		DE-D-	3750750	15-12-94
		DE-A-	3780411	20-08-92
		EP-A, B	0268353	25-05-88
		ES-T-	2063424	01-01-95
		JP-C-	1726923	19-01-93
		JP-B-	4005486	31-01-92
		JP-A-	63130125	02-06-88
EP-A-0463367	02-01-92	US-A-	5118480	02-06-92
EP-A-0573209	08-12-93	NONE		
EP-A-0314253	03-05-89	US-A-	4865627	12-09-89
		AU-B-	606761	14-02-91
		AU-A-	2448788	04-05-89
		CA-A-	1315710	06-04-93
		DE-A-	3877325	18-02-93
		JP-A-	1148323	09-06-89